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<b>(21) International Application Number:</b> PCT/FI94/00080 <b>(22) International Filing Date:</b> 4 March 1994 (04.03.94) <b>(30) Priority Data:</b> 930980 5 March 1993 (05.03.93) FI <b>(71) Applicant (for all designated States except US):</b> VALTION TEKNILLINEN TUTKIMUSKESKUS [FI/FI]; c/o Otatech Ltd., P.O. Box 402, FIN-02151 Espoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HASE, Anneli [FI/FI]; Mannerheimintie 37 B 41, FIN-00250 Helsinki (FI). ALA- PEIJARI, Maija [FI/FI]; Kuninkaanlahdentie 13 A, FIN- 02160 Espoo (FI). AALTONEN, Olli [FI/FI]; Eino Leinon katu 10 A 10, FIN-00250 Helsinki (FI). HASE, Tapio [FI/FI]; Rikhardinkatu 4C, FIN-00100 Helsinki (FI). <b>(74) Agent:</b> HARTIKAINEN, Liisa; Otatech Ltd, P.O. Box 402, FIN-02151 Espoo (FI).		<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> METHOD FOR OXIDATION  <b>(57) Abstract</b>  The invention relates to a method for the direct oxidation of benzene into phenols. In the method according to the invention benzene is dissolved in a mixture of supercritical carbon dioxide, molecular oxygen, and hydrogen. Oxidation occurs at a temperature not less than 50 °C and at a pressure not less than 77 bar using a Pd-containing catalyst.		

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## METHOD FOR OXIDATION.

The object of the present invention is a method for oxidation of aromatic hydrocarbons such as benzene into phenols in a single step. In the method according to the invention, molecular oxygen is used as an oxidizing agent, and carbon dioxide in supercritical state is used as a reaction medium. Palladium-containing heterogeneous catalysts are used. Reaction mixture contains also reducing gas, for example hydrogen.

The direct oxidation of aromatic hydrocarbons into phenols is a method which, when successful, will have a great economical importance for the modern petrochemical industry. However, for instance all the direct oxidation methods of benzene known so far are unsatisfactory and therefore none of them is in industrial use.

For example, the oxidation of benzene with peroxides and metal ions in aqueous solutions is known (Acc. Chem. Res., 1975, Vol. 8, p. 125). Since benzene is very sparingly soluble in water, this method is inefficient.

It is also known (J. Phys. Chem., 1983, Vol. 87, p. 903 and JP 61236738) that benzene may be oxidized with nitrous oxide in the presence of water. Despite the vanadium oxide catalyst used the required reaction temperature is 550 °C.

Furthermore, it is known (Catal. Lett., 1990, Vol. 4, p. 139) that the oxidation of benzene may be carried out with gaseous oxygen in the presence of hydrogen using palladium or palladium-copper composite catalysts. However, oxidation carried out as a gas-phase or liquid-phase reaction stops at a very low level of yield.

Carbon dioxide in supercritical state has been successfully tested as a reaction medium for instance in several enzyme-catalyzed reactions (Chemtech 1991, p. 240) and in hydroformylation (Organometallics 1991, Vol. 10, p. 1350). Carbon dioxide is in a supercritical state when its temperature is higher than the critical temperature of carbon dioxide (31.1 °C) and when the pressure simultaneously is higher than the corresponding critical pressure (73.8 bar). Carbon dioxide in supercritical state is a good solvent for hydrocarbons and a very good solvent for gases. The viscosity of supercritical carbon dioxide is low and diffusibility is high compared to liquid solvents. Furthermore, since the surface tension between supercritical carbon dioxide and liquids is very low, it could be expected that particularly reactions limited by mass transfer, would proceed better in carbon dioxide than in liquid solvents. However, in the oxidation of cumene (Ind. Eng. Chem. Res., 1989, Vol. 28, p. 1152) and toluene (Ind.

Eng. Chem. Res., 1987, Vol. 26, p. 1910), for instance, no advantages have been obtained of the use of supercritical carbon dioxide compared to the use of liquid solvents.

5 We have observed that by dissolving an aromatic hydrocarbon such as benzene in carbon dioxide in supercritical state wherein molecular oxygen has been mixed, and maintaining thus obtained reaction mixture in contact with a suitable catalyst, the oxidation of benzene into phenol is achieved with a significantly higher yield than proceeding according to the known methods.

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The invention allows the embodiment of a new production method of phenols.

The advantages of the method according to the invention are:

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- Aromatic hydrocarbons and oxygen dissolve well in supercritical carbon dioxide. Reaction mixture is homogeneous. The use of an inefficient two-phase system is avoided.

- The required reaction temperature is lower than in certain known oxidation methods.

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- The yield of phenols is higher than the one obtained when proceeding according to the known methods.

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- The major component of the reaction mixture is carbon dioxide. It is inexpensive, noninflammable and nontoxic. This brings benefits as savings in preventing hazards due to solvent emissions. A plant using carbon dioxide as a solvent does not cause any harmful solvent emissions to the environment.

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- The carbon dioxide separated from the reaction mixture is vaporized and can be led to the oxidation of a new batch of aromatic hydrocarbons after being pressurized and temperature-controlled. Because of the low vaporization heat of carbon dioxide, the energy needed for carbon dioxide recycling of is only a fraction of the energy needed for the recycling of organic solvents. The use of the method according to the invention thus brings in a considerable saving in the operating costs.

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The method according to the invention is characterized in that the aromatic hydrocarbon to be oxidized is dissolved in the gas mixture where the major component is carbon dioxide in supercritical state. The gas mixture contains a reducing gas and as oxidizing agent molecular oxygen. Pd-containing catalysts are used as oxidizing catalysts. The oxidation is carried out most preferably at a temperature in the range

between 50 and 113 °C. The reaction pressure is preferably in the range of 77 to 102 bar. The reaction time is preferably not higher than 3 hours.

The following examples illustrate the invention.

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### Examples

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45 mg of solid catalyst, 8 microliters of water, and 2 ml of benzene were introduced in a steel autoclave of a volume of 80 ml. Pd catalysts were prepared by precipitation of palladium chloride from an aqueous solution onto the surface of silica gel particles (230 - 400 Mesh). Pd-Cu composite catalysts were prepared by precipitating palladium chloride and copper sulphate simultaneously on the silica gel particles.

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Mixtures of carbon dioxide and reactant gases were prepared in a second autoclave with a volume of 80 ml. The mixtures of oxygen and hydrogen were purged into the reactor with pressurized carbon dioxide from the mixing vessel for the gases.

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Reactions were initiated by heating the reactor in 10 minutes to the experimental temperature. Reactor content was mixed with a magnetic bar. The reaction was terminated by cooling the whole reactor in an ice-water bath. The reactor was opened and carbon dioxide was allowed to evaporate. Reactor content was analyzed by gas chromatography.

Experimental results are summarized in the following table.

Experiment	The end composition of the reaction mixture				Reaction conditions		Reaction time	Reaction gas mixture	
	PH	CH	CA	HQ	T	p	t	O <sub>2</sub>	H <sub>2</sub>
	mg/ml	mg/ml	mg/ml	mg/ml	°C	bar	h	%-vol.	%-vol.
1	2.2	0.3			49	87	16	2	2
*2	3.8	1.1			50	101	3	3	3
3	1	0.1			57	77	16	2.5	1
4	1.8	0.2	0.13	0.01	58	83	3	4	1
5	0.8	0.1			58	102	3	2.5	1.3
6	4.9	0.8	0.2	0.01	78	83	3	3.6	2
7	6	1	0.2	0.02	78	93	3	2.6	2
8	2.6	0.3	<0.01	0.03	88	97	3	4	1
9	6	1.2	0.1	0.03	98	91	3	3.6	2
10	5.2	1	0.2	0.01	99	91	1	3.6	2
11	1.8	0.6	0.02	0.01	99	93	18	3.6	2
**12	0.9	0.6	0.03	0.03	99	94	3	3.6	2
13	6.1	0.6	0.2	0.04	101	87	3	4	2
14	3.3	0.6	0.03	0.01	113	91	3	3.6	2
15	3.4	0.8	0.03	0.01	113	102	3	4.2	2.4

PH=phenol, CH=hydrogenated products, cyclohexanone and cyclohexanol,  
CA=cathecol, HQ=hydroquinone

\* 100 mg of catalyst (45 mg in all the other experiments)

\*\*Cu-Pd composite catalyst (Pd catalyst on silica in all the other experiments)

**Claims:**

- 5 1. Method for the preparation of phenols by direct oxidation of benzene characterized in that a homogeneous reaction mixture is formed of benzene, carbon dioxide, molecular oxygen and reducing gas at elevated pressure and temperature in which mixture there is no liquid phase and which is contacted with a solid catalyst.
- 10 2. Method according to the claim 1 characterized in that the oxygen content in the gas mixture is 2 - 4.2 % by volume.
3. Method according to the claim 1 characterized in that the solid catalyst is a palladium catalyst prepared on a silica support.
- 15 4. Method according to the claim 1 characterized in that the period of time during which the reaction mixture is in contact with the solid catalyst is not more than 3 hours.
5. Method according to the claim 1 characterized in that the content of the reducing gas in the gas mixture is 1 - 3 % by volume.
- 20 6. Method according to the claim 1 characterized in that the temperature of the reaction mixture is not less than 49 °C.
- 25 7. Method according to the claim 1 characterized in that the pressure in the reaction mixture is not less than 77 bar.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00080

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC 5: C07C 37/58, C07C 39/04 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
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<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	IND.ENG.CHEM.RES., Volume 26, 1987, Kerry M. Dooley et al, "Oxidation Catalysis in a Supercritical Fluid Medium" page 1910 - page 1916 --	1-7
A	IND.ENG.CHEM.RES., Volume 28, 1989, Galen J. Suppes et al, "Oxidation of Cumene in Supercritical Reaction Media" page 1152 - page 1156 --	1-7
A	CATALYSIS LETTERS, Volume 4, 1990, Atsutaka Kunai et al, "Pd/SiO <sub>2</sub> catalyst for oxidation of benzene to phenol" page 139 - page 144 -----	1-7
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